Li intercalation effects on magnetism in undoped and Co-doped anatase TiO_2

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Abstract

The effects of n-type carrier doping by Li intercalation on magnetism in undoped and Co-doped anatase TiO_2 are investigated. We have found that doped n-type carriers in TiO_2 are localized mainly at Ti sites near the intercalated Li. With increasing the intercalation, local spins are realized at Ti. In the case of Co-doped TiO_2, most of the added n-type carriers fill the Co $3d$ bands and the rest are localized at Ti. Therefore, Co magnetic moment vanishes by Li intercalation to have a nonmagnetic ground state.

Keywords: Dilute magnetic semiconductor; Electronic structure; TiO_2

Anatase TiO_2 is a wide band gap (3.2 - 3.7 eV) semiconductor. This wide band gap property provides a wide range of applications, such as air and water purifications using photocatalysis which converts solar energy into electrochemical energy [1] and batteries, electrochromic devices based on lithium intercalation. A theoretical study [2] shows that Li intercalation is easier in anatase TiO_2 than in rutile TiO_2. This is due to the open structure of anatase TiO_2. Recently, magnetic features are observed in the Li intercalated anatase TiO_2 [3]. It is possible to intercalate Li atoms up to Li/Ti ratio $\sim$ 0.7. With increasing the Li intercalation, a structural transition occurs from tetragonal to orthorhombic one. Also the insulator-to-metal transition is observed for $x>$ 0.3. The localized moments were measured, 0.003 $\sim$ 0.004μ_B per Ti, through the Li intercalation.

On the other hand, room temperature ferromagnetism is observed in Co-doped anatase TiO_2 thin film made by the combinatorial pulsed-laser-deposition molecular-beam epitaxy method [4]. A sizable amount of Co, up to 8%, is soluble in anatase TiO_2. The measured saturated magnetic moment per Co ion was $0.32\mu_B$ apparently in the low spin state and T_C was estimated to be higher than 400 K. It is recognized that the carriers play role of inducing the ferromagnetism in dilute magnetic semiconductors [5].

To explore the carrier doping effects on magnetism, we have investigated electronic and magnetic properties of Li intercalated anatase TiO_2 and $Ti_{1-x}Co_xO_2$ (x=0.0625). Li/Ti intercalation ratios of 0.0625, 0.125, and 0.25 are considered for the undoped case, while 0.067 and 0.133 for the Co-doped case. We consider only the tetragonal anatase structure. We have used the linearized muffin-tin orbital (LMTO) band method in the local-spin-density approximation (LSDA). We have considered a supercell containing 16 f.u. in the primitive unit cell by replacing one Ti by Co or intercalating several Li ions (a=b=7.570, c=9.514 Å). Sixteen empty spheres are employed at the interstitial sites to enhance the packing ratio in the LMTO band calculation.

We have first calculated the electronic structure of Li intercalated TiO_2. In all Li/Ti ratio cases, we have obtained metallic ground states (Fig. 1). For Li/Ti=0.0625, the paramagnetic ground state is obtained. However, in other cases, total energies of the paramagnetic

and the ferromagnetic ground state are almost the same. Doped n-type carriers fill the Ti $3d$ conduction band. Maximum localized magnetic moments at Ti are 0.029, 0.027 μ_B for Li/Ti=0.125 and 0.25, respectively. Thus the magnetic moment is not necessarily proportional to the number of localized electrons at Ti. The exchange splitting is clearly seen in the valence band top mainly with O $2p$ characters (Fig. 1).

Now, we have performed band calculations for Co-doped case. For Li/Ti=0.067, we have obtained paramagnetic and insulating ground state in Fig. 2. Insulating ground state results from filling up Co $3d$ band by the n-type carriers. Therefore, Co t_{2g} band is fully occupied, and the total occupancy of d states amounts to $d^7(t_{2g}^6 e_g^1)$. As seen in Fig. 2, the position of occupied t_{2g} band is different from the non-intercalated Co-doped case. In the latter case, the occupied Co t_{2g} band is located near the valence band top [6], while, in the former case, the fully occupied Co t_{2g} band is located near the conduction band bottom. The unoccupied Co e_g band is hybridized with Ti $3d$ conduction band.

For the Li/Ti=0.133 case, nearly paramagnetic and metallic ground state is obtained (Fig. 2). The carriers are mainly of Ti $3d$ character. The extra electrons after filling up the Co t_{2g} band occupy not Co e_g band but Ti $3d$ conduction band, because the carriers are localized at Ti sites near the intercalated Li. From these, one can expect that n-type carrier induced ferromagnet can be fabricated in TiO_2 by simultaneously intercalating Li and doping some $3d$ transition metals having high spin magnetic ground state such as Mn, Fe [6].

In conclusion, we have found that, by intercalating Li in TiO_2, Ti atoms have localized magnetic moments, 0.029 and 0.027μ_B for Li/Ti=0.125 and 0.25, respectively. In the case of Co-doped TiO_2, nonmagnetic ground states are obtained for Li/Ti=0.067 and 0.133.

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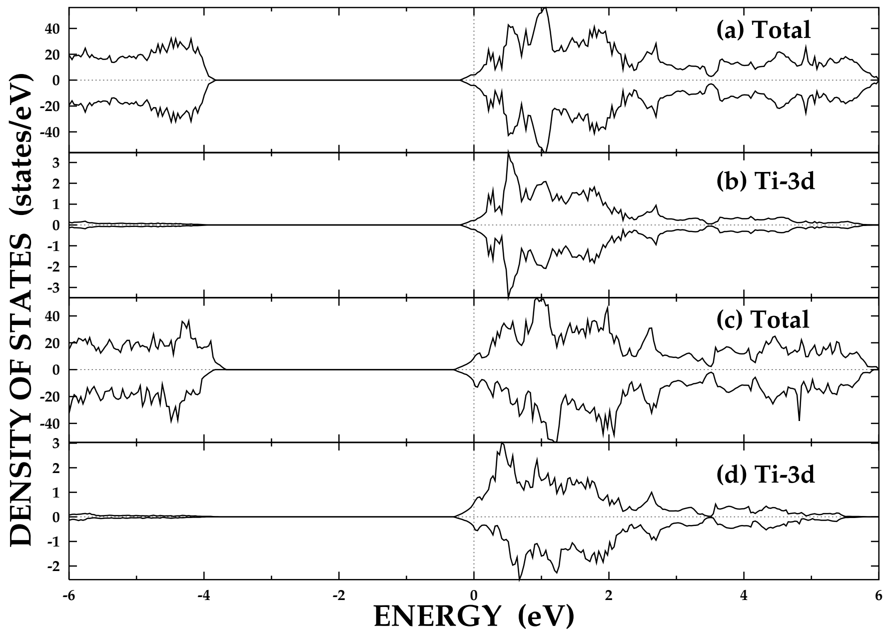
FIGURES

FIG. 1. The LSDA total and projected local density of states (PLDOS) of Li intercalated TiO_2 ((a),(b) : Li/Ti=0.0625, (c),(d) : Li/Ti=0.125)

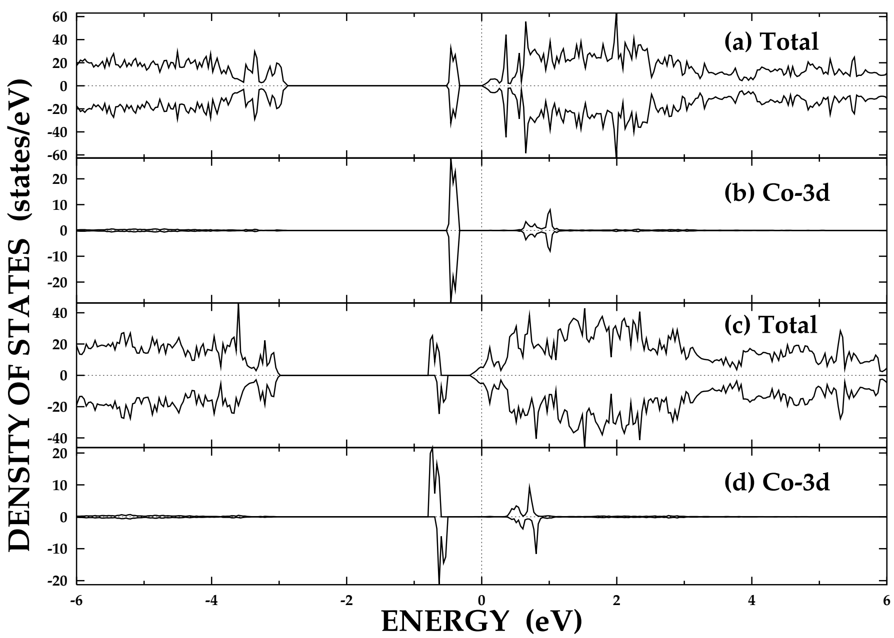
FIG. 2. The LSDA total and PLDOS of Li intercalated $Ti_{1-x}Co_xO_2$ (x=0.0625) ((a),(b) : Li/Ti=0.067, (c),(d) : Li/Ti=0.133)

Fig.1



(a) Total
(b) Ti-3d
(c) Total
(d) Ti-3d
DENSITY OF STATES (states/eV)
ENERGY (eV)

Fig.2



(a) Total
(b) Co-3d
(c) Total
(d) Co-3d
DENSITY OF STATES (states/eV)
ENERGY (eV)